

Geochemical features of aerosols in Santiago de Chile from time series analysis

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Abstract Santiago, the capital of Chile, suffers from high air pollution levels, especially during winter. An extensive particulate matter (PM) monitoring and analysis program was conducted to quantify elemental concentrations of PM. Size-resolved PM samples (PM_{2.5} and PM_{10–2.5}) from the La Paz and Las Condes stations in Santiago (2004–2005) were analyzed using ICP-MS. Most trace element concentrations (Cu, Pb, Zn, Mn, V, Sb, Pb and As) were higher during winter than during summer and were also higher at the La Paz station than at the Las Condes station. During the highest pollution events, As concentrations in PM_{2.5} (16 ng m^{−3}) exceeded the annual average standard value (6 ng m^{−3}). A 10-year time series showed decreasing Pb and As concentrations and slightly increasing Zn, Cu and Mn concentrations. Concentrations of Cr and Ni remained relatively constant. The implementation of new public policies in 1998 may explain the decreasing concentrations of Pb and As. Enrichment factor (EF) calculations identified two principal groups: elements with EF < 10 (Mg, Y, Zr, U Sr, Ca, Ti, and

V) and EF > 10 (Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn, Sn, Pb, Cu, Mo, Cd, As, Ag, and Sb), which were related to natural and anthropogenic PM sources, respectively. Three main PM sources were identified using factor analysis: a natural source (crustal matter and marine aerosol), combustion and copper smelting. Three other sources were identified using rare earth elements: fluid catalytic crackers, oil-fired power production and catalytic converters.

Keywords Geochemistry · Particulate matter · Source · Pollution · Trace element

Introduction

Santiago has experienced rapid urban, industrial and demographic growth (Romero et al. 1999). As a consequence, there has been an increase in public and private transportation and industries. In fact, in 2007, the number of vehicles in Santiago reached 1.2 million and from 2003 to 2007 a net increase in exportation was apparent, reflecting 100 % growth of the industrial sector and more than 1,000 % growth in the mining sector (Centro Mario Molina Ltda. 2008). As a consequence of this growth, particulate matter (PM) emissions have increased from these sources, contributing to persistent atmospheric pollution. This phenomenon is typical of Latin American megacities like Santiago, Sao Paulo and Mexico City, and can have a serious impact on the population's health. In Santiago, aside from the well-known roles of gases and organic carbon, few studies have identified trace element concentrations of PM (Artaxo et al. 1999), despite their role in respiratory and cardiovascular diseases (Cakmak et al. 2009; Valdés et al. 2012).

The meteorological and topographical features of Santiago contribute to high concentrations of PM that fluctuate

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throughout the year (average PM_{10} concentration of $300 \mu\text{g m}^{-3}$), with especially high concentrations ($\sim 500 \mu\text{g m}^{-3}$) occurring in winter (Jorquera et al. 1998; Artaxo et al. 1999).

A clean air plan in Santiago (PPDA) (Lents et al. 2006), implemented in 1998, aimed to decrease the concentrations of major pollutants (PM_{10} , O_3 , NO_x , SO_2 , and CO_2) through the removal of fixed pollution sources (diesel generators, waste burning, large wood and, coal burning), improving the transportation fleet and the introduction of catalytic converters for new vehicles. However, from 2004 to 2005, PM_{10} concentrations began to increase. This was likely related to specific meteorological conditions, such as El Niño or energy matrix modification, and an increase in Chile's production activity.

This study aimed to present a detailed geochemical (major and trace elements) characterization of urban PM in Santiago. A 2-year time series (2004–2005) of $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ samples were collected at two monitoring sites, La Paz (LP) and Las Condes (LC), which were representative of the contrasting conditions that can occur in Santiago. These stations were selected to identify the influence of local PM sources and their effects on PM concentrations. The LP station was located in the center of Santiago in a mixed (industrial/residential/commercial) district. It was surrounded by four main roads featuring heavy traffic, a crematorium and various boilers, small-scale industries and power-supply installations. The LC station was in a residential area partly covered with vegetation. Few potential sources, such as boilers, heaters and power generators, were located in its surroundings.

The data obtained were analyzed by source (natural versus anthropogenic) and contaminant origin, as supported by a previous mineralogical study (Morata et al. 2008). Chemical signatures were also compared with previously published data in Santiago (Artaxo 1998) and in central Chile (Hedberg et al. 2005) to better identify temporal changes in the atmospheric contamination over Santiago.

Santiago general context

Geography and climate

Santiago (33.5°S , 70.8°W) is a metropolis of around 6 million inhabitants located 450–750 m above sea level (asl) within a confined basin between the Andes Cordillera ($>4,500$ m asl) and the Coastal Range ($<2,000$ m asl) (Fig. 1). Yearly rainfall is typically less than 312 mm (<http://164.77.222.61/climatologia/>) and temperatures range from -2 to 35°C , with average temperatures of approximately 10 and 20°C during the winter and summer,

respectively. High-pressure, anticyclonic conditions prevail in central Chile all year long and lead to stable, warm and sunny weather. Low-pressure conditions are associated with rain and cold air masses. On most days, an inversion layer prevents both vertical air movement and mixing between air masses, producing optimal conditions for the accumulation of polluted air (Romero et al. 1999). Regional NE–SW winds are dominant and are much stronger during the day, allowing the horizontal transport of pollutants within the basin (Rutllant and Garreaud 1995). Extreme air pollution events typically occur from April to August, when inversion layers as low as 150 m trap pollutants inside the city, leading to extremely high PM_{10} concentrations ($\sim 500 \mu\text{g m}^{-3}$).

Main features of atmospheric pollution in Santiago

Air pollution in Santiago results from a combination of natural and anthropogenic sources (Jorquera 2002). Natural sources include resuspended dust from eroded remote areas and from soils within the city, and marine (sea spray) and biogenic sources (pollens). Anthropogenic sources can be grouped according to major industrial activities: power plants, chemical industries, oil refineries, metallurgy and mining activities that include the ore deposit, El Teniente, and its copper smelter. Three copper smelters, at Caletones (90 km south of Santiago), Ventanas (119 km northwest of Santiago) and Chagres (98 km northwest of Santiago) are high SO_2 and volatile metal (Cu, Zn, As, Mo, and Pb) emitters that affect central Chile (Romo-Kröger et al. 1994; Kavouras et al. 2001; Garcia-Huidobro et al. 2001) and Santiago (Gallardo et al. 2002) (Fig. 1).

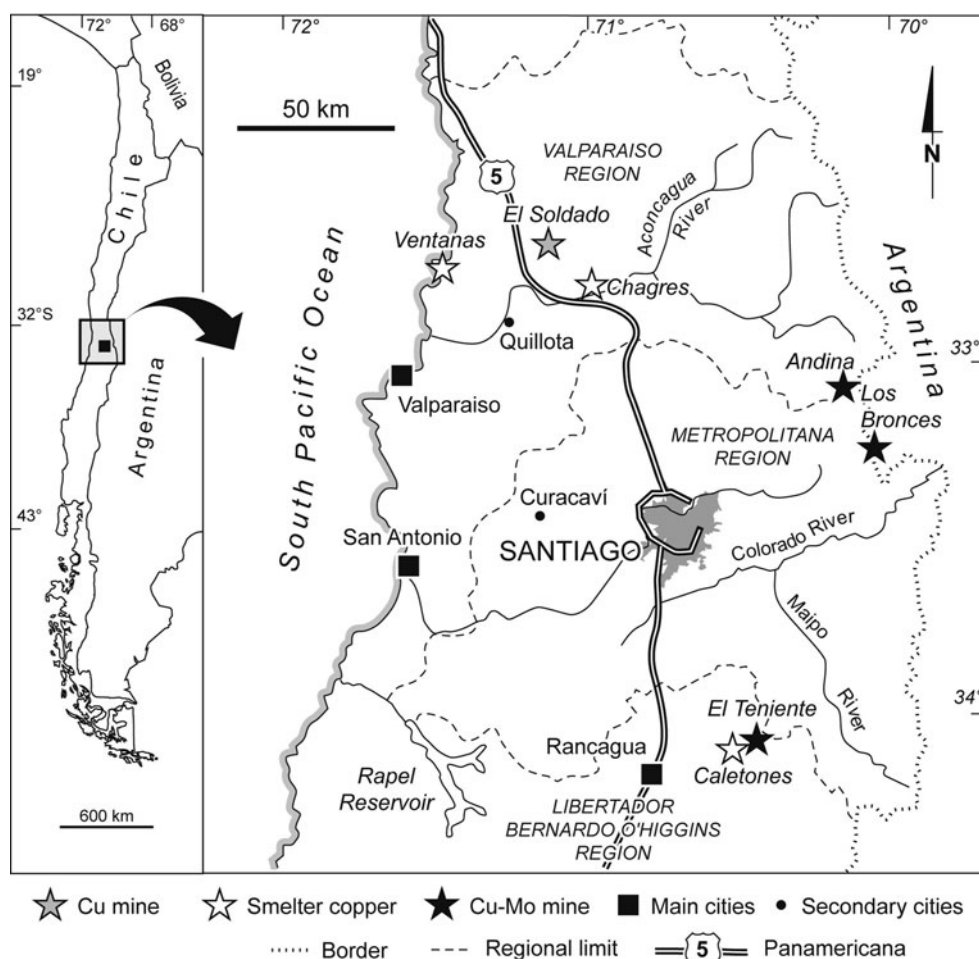
Sampling sites and methods

The PM filters were supplied by the Air Quality Monitoring Network (MACAM NET, Santiago). MACAM operates eight stations distributed over the metropolis with automatic and semi-automatic monitoring systems for CO , SO_2 , O_3 , and particulate matter. Three of the sites make continuous measurements of NO_3 , temperature, humidity, solar radiation and wind direction.

Samples were collected using a dichotomous sampler (Sierra Andersen 244, Smyrna, GA) on 4 cm diameter Pall-Flex Teflon filters. This sampler collects particles with sizes less than $2.5 \mu\text{m}$ (fine fraction, $\text{PM}_{2.5}$) and between 2.5 and $10 \mu\text{m}$ (coarse fraction, $\text{PM}_{10-2.5}$) under a bulk flow rate of $16\text{--}18 \text{ L min}^{-1}$. The sampling time was 24 h for each of the samples.

During autumn and winter, samples were collected from 10:00 am to 10:00 am, and during spring and summer, samples were collected from midnight to midnight. Samples

Fig. 1 Map of the study area showing main roads, cities, mines and smelters. The region termed central Chile is made up of the cities or localities of Ventanas, Chagres, Valparaíso, Santiago and Rancagua



were collected daily from April to September, every 2 days in October, November and March, and every 3 days from December to February, 1998–2007. The monitoring frequencies were based on pollution concentrations during the year and were decided on by the National Environment Commission. Daily monitoring in the colder months (April–September) was consistent with higher PM concentrations and less frequent sampling was performed in the warmer seasons because of better ventilation conditions.

A total of 202 samples from the LC and LP stations (Fig. 2) were analyzed among the filters collected from 2004 to 2005 by MACAM. Filters were weighed before and after sampling using a $\pm 1 \mu\text{g}$ microbalance and were stored in sterile Petri dishes kept inside dry chambers under controlled humidity and temperature conditions.

Analytical techniques

Major and trace elements analyses were carried out at GET (Laboratoire de Géosciences Environnement, Toulouse, France) in a class 1,000 clean room. Filters were cut into

four sections using a clean ceramic knife and Teflon tools to reduce the risks of contamination. Three of the sections were stored for complementary analyses. Filter sections were digested in 7 mL Teflon beakers. First, 100 μL of triple-distilled methanol and 200 μL of double-distilled 14N HNO_3 were added to the sample, which was left on a hot plate for 12–24 h at 100 °C after being ultrasonicated for 15 min. After heating, 100 μL of ultraclean 15N HF and 200 μL of 14N HNO_3 were added and the beakers were heated at 150 °C for 48 h. Digestion was usually complete and remaining liquid was evaporated at 50 °C. The dry residue was recovered with 50 μL of 14N HNO_3 . An internal standard solution (In and Re) and ultrapure water were added to produce 2 mL of a 0.37N HNO_3 final solution. This final solution was analyzed using ICP-MS (Agilent 7500).

The ICP-MS system was equipped with a collision cell. Elements were identified using at least two isotopes, where possible, under two different analytical modes, with or without gas in the collision cell. Indium was used as the internal standard and Re was used as a control of the validity of this standardization. External calibration was

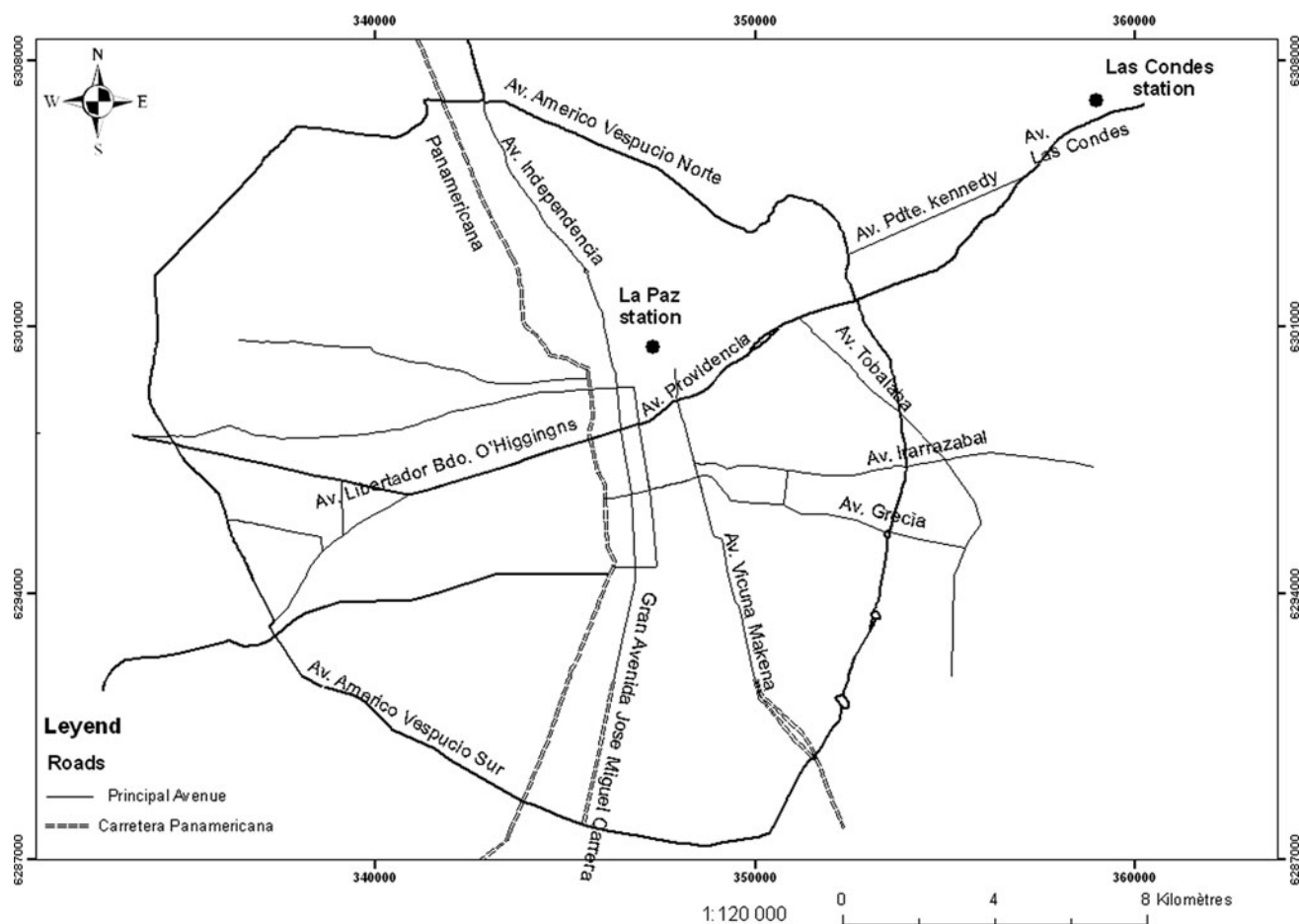


Fig. 2 Main roadways in Santiago with the locations of the two monitoring stations shown

performed using non-matrix-matched solutions made in the laboratory. The protocol used for the internal standard preparation and interference correction was based on a previous report by Aries et al. (2000).

The 202 analyzed samples corresponded to 102 $PM_{2.5}$ samples and 100 $PM_{10-2.5}$ samples. After ICP-MS analysis, data for 48 elements that had at least 80 % of their concentrations above the detection limit ($DL = 3 \times$ standard error of analytical blanks) were used for further analyses. These elements included major elements (Na, Mg, Al, K, Ca, and Fe), trace elements (P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, Mn, As, Sr, Rb, Zr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Hf, Ta, and W) and rare earth elements from La to Lu. The average blank contribution to elemental concentrations was approximately 10 % for most elements. It reached 15 % for Mg, Sc, Co, Sr, Nd, Sm, and Th and ranged from 20 to 80 % for P, Ca, Cr, Ni, Zn, Sb, Hf, W, and U in 50–75 % of the samples, indicating much higher uncertainties in the concentrations of these elements.

To validate the analyses, 12 duplicates from randomly chosen samples were analyzed using a separate fraction of

each filter that underwent the complete analytical process. Differences among the elemental concentrations between the two filter samples were calculated using:

$$[(X - Y) \times 2 / (X + Y)] \times 100, \quad (1)$$

where X is the concentration of the given element in the duplicate sample and Y is the concentration of that element from the first analysis. Concentrations of the major elements Na, Al, K, Ca, and Fe differed by 50 %, while Mg and Ti showed much better reproducibility. Percentage differences were as low as 17 % (Zn) and 0 % (As, Pb, and Mo) for the trace elements, especially in $PM_{2.5}$. Elemental recoveries from 83 to 100 % were consistent with those observed by Jalkanen and Häsänen (1996). Accuracy differences among major and trace elements indicated that the dilution process was not sufficiently complete for the major elements in comparison to the trace elements (Yong-Keun et al. 1991). Conversely, similar digestion processes have shown that increasing the amount of HF used decreased the method accuracy for lighter elements from Zn to V (Swami et al. 2001). However, the use of HF increased the recovery

Table 1 Average PM_{10–2.5}, PM_{2.5} and elemental concentrations by season

Station:	La Paz				Las Condes			
PM:	PM _{2.5}		PM _{10–2.5}		PM _{2.5}		PM _{10–2.5}	
Season:	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
PM (μgm^{-3}):	61.4	19.5	48.2	32.0	47.9	19.5	30.0	31.5
Elements (ngm^{-3})								
Na	133.9	196.7	304.4	349.1	110.5	231.7	298.2	243.1
Mg	46.9	25.7	132.5	89.4	32.2	32.7	131.0	62.9
Al	155.1	83.6	850.4	588.8	141.7	61.1	564.7	364.7
P	24.8	12.4	36.4	23.8	18.9	11.9	19.1	14.2
K	194.9	188.9	258.8	166.5	219.5	169.5	180.8	121.4
Ca	411.6	244.8	931.0	504.1	304.8	351.2	963.0	445.8
Sc	0.02	0.02	0.2	0.1	0.02	0.02	0.1	0.1
Ti	12.3	4.2	80.1	73.2	21.4	4.3	53.4	23.1
V	0.8	0.4	2.1	1.3	0.7	0.3	1.2	0.7
Cr	5.1	2.1	5.8	42.8	24.6	2.1	3.3	1.0
Mn	22.3	10.9	31.3	22.5	12.4	12.0	13.2	12.9
Fe	355.4	118.8	1063.6	601.5	283.8	62.4	558.8	264.2
Co	3.1	4.4	2.7	2.1	7.5	9.1	3.6	3.6
Ni	1.9	8.2	2.2	148.2	26.8	1.3	2.3	0.9
Cu	26.5	8.2	27.7	10.9	18.5	5.1	18.3	5.6
Zn	79.2	13.4	39.0	18.5	45.1	7.4	24.2	5.5
Ga	0.17	0.04	0.25	0.15	0.12	0.03	0.14	0.09
Ge	0.07	0.01	0.04	0.01	0.04	0.01	0.02	0.01
As	4.6	1.0	1.2	0.3	4.8	1.2	0.8	0.3
Rb	0.4	0.3	0.8	0.6	0.4	0.2	0.5	0.3
Sr	1.5	0.8	5.6	2.9	1.0	0.9	4.2	1.9
Y	0.1	0.0	0.2	0.2	0.1	0.0	0.2	0.1
Zr	0.8	0.4	3.4	1.7	0.9	0.2	1.7	0.6
Mo	2.1	1.3	3.7	2.8	2.4	0.7	2.9	1.2
Ag	0.4	0.1	0.2	0.1	0.2	0.1	0.3	0.04
Cd	0.5	0.1	0.1	0.0	0.3	0.1	0.0	0.01
Sn	5.0	3.1	1.7	0.5	3.3	0.8	1.1	0.2
Sb	17.2	22.6	17.4	54.3	30.6	45.6	17.5	46.2
Cs	0.03	0.01	0.1	0.05	0.03	0.01	0.05	0.03
Ba	25.2	10.2	57.2	17.7	11.4	2.9	20.9	6.3
La	0.141	0.056	0.294	0.157	0.088	0.032	0.173	0.094
Ce	0.300	0.106	0.754	0.364	0.175	0.053	0.384	0.204
Pr	0.022	0.010	0.064	0.039	0.015	0.005	0.040	0.023
Nd	0.078	0.027	0.247	0.150	0.053	0.015	0.180	0.090
Sm	0.012	0.006	0.050	0.032	0.009	0.003	0.033	0.019
Eu	0.006	0.002	0.019	0.010	0.004	0.001	0.010	0.005
Gd	0.015	0.007	0.058	0.035	0.012	0.004	0.037	0.021
Tb	0.005	0.001	0.012	0.005	0.006	0.0004	0.010	0.003
Dy	0.005	0.004	0.036	0.027	0.004	0.003	0.023	0.016
Ho	0.004	0.001	0.010	0.005	0.004	0.0004	0.008	0.003
Er	0.003	0.002	0.021	0.016	0.002	0.002	0.013	0.009
Yb	0.005	0.002	0.022	0.014	0.004	0.001	0.015	0.009
Hf	0.030	0.009	0.078	0.033	0.029	0.003	0.042	0.012
W	0.207	0.062	0.268	0.076	0.152	0.016	0.147	0.033

Table 1 continued

Station:	La Paz				Las Condes			
PM:	PM _{2.5}		PM _{10–2.5}		PM _{2.5}		PM _{10–2.5}	
Season:	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
PM (μgm^{-3}):	61.4	19.5	48.2	32.0	47.9	19.5	30.0	31.5
Pb	26.1	4.3	11.0	3.0	16.5	2.8	4.6	1.2
Bi	0.137	0.023	0.051	0.016	0.117	0.031	0.050	0.013
Th	0.026	0.003	0.066	0.018	0.030	0.001	0.049	0.009
U	0.010	0.010	0.027	0.011	0.034	0.003	0.017	0.007

of Cr (by $\sim 30\%$). Poor elemental recoveries probably result from particles being covered in layers of soot and organic matter (Jalkanen and Häsänen 1996). Elements in the fine particle fraction had better reproducibilities than those in the coarse fraction at both stations because of greater heterogeneity of the coarse particles.

Results and discussions

Results from the 2-year monitoring of PM_{2.5} and PM_{10–2.5} are presented in Table 1 as seasonal averages of PM ($\mu\text{g m}^{-3}$) and elemental concentrations (ng m^{-3}). The values presented in Table 1 are the average concentrations of 3–5 samples selected at random according to season from the MACAM monitoring network MACAM. The samples featured days with high, moderate and low PM concentrations in each month. Maximum PM concentrations occurred during autumn and winter. From 2004 to 2005, 25 days experienced PM₁₀ concentrations higher than $200 \mu\text{g m}^{-3}$ and samples from 14 of those days were analyzed in this study.

Total PM concentrations

Seasonal variations

At both monitoring stations seasonal trends were apparent, similar to results from 1996 and 2005 by Artaxo et al. (1999) and Gramsch et al. (2006), respectively. Higher average concentrations were measured during winter at both stations. Time series of PM_{2.5}/PM_{10–2.5} ratios also displayed clear seasonal trends, with ratios higher than 1 (PM_{2.5} > PM_{10–2.5}) during the cold season from April to September. Short-term fluctuations with an abrupt decrease in concentrations could be linked to rainfall events that wash out pollutants and decrease the re-suspension of coarse particles from ground and soil erosion (Fig. 3). For example, from 29 July to 3 August 2004 and 22–27 June

2005, the precipitation measured was 24.4 and 62.1 mm, respectively (<http://164.77.222.61/climatologia/>). Major elemental concentrations decreased by between 65 and 86 % in 2004 and between 87 and 98 % in 2005. Trace element concentrations decreased by approximately 90 % in both years.

The similarities observed among bulk concentrations and PM_{2.5}/PM_{10–2.5} ratios suggest that the same processes control their variations. The seasonal effect likely resulted from a drastic reduction of atmospheric turbulence and a decrease in the mixing layer during colder months, which reduces PM dispersion and subsequently, increases PM concentrations. High elemental concentrations and PM_{2.5}/PM_{10–2.5} ratios are correlated with prevailing low wind speeds during the winter in central Chile (Sandoval et al. 1993). PM and elemental concentrations were found to be higher during the cold season than during the warm season, except for Sb and Na, which displayed the opposite trend.

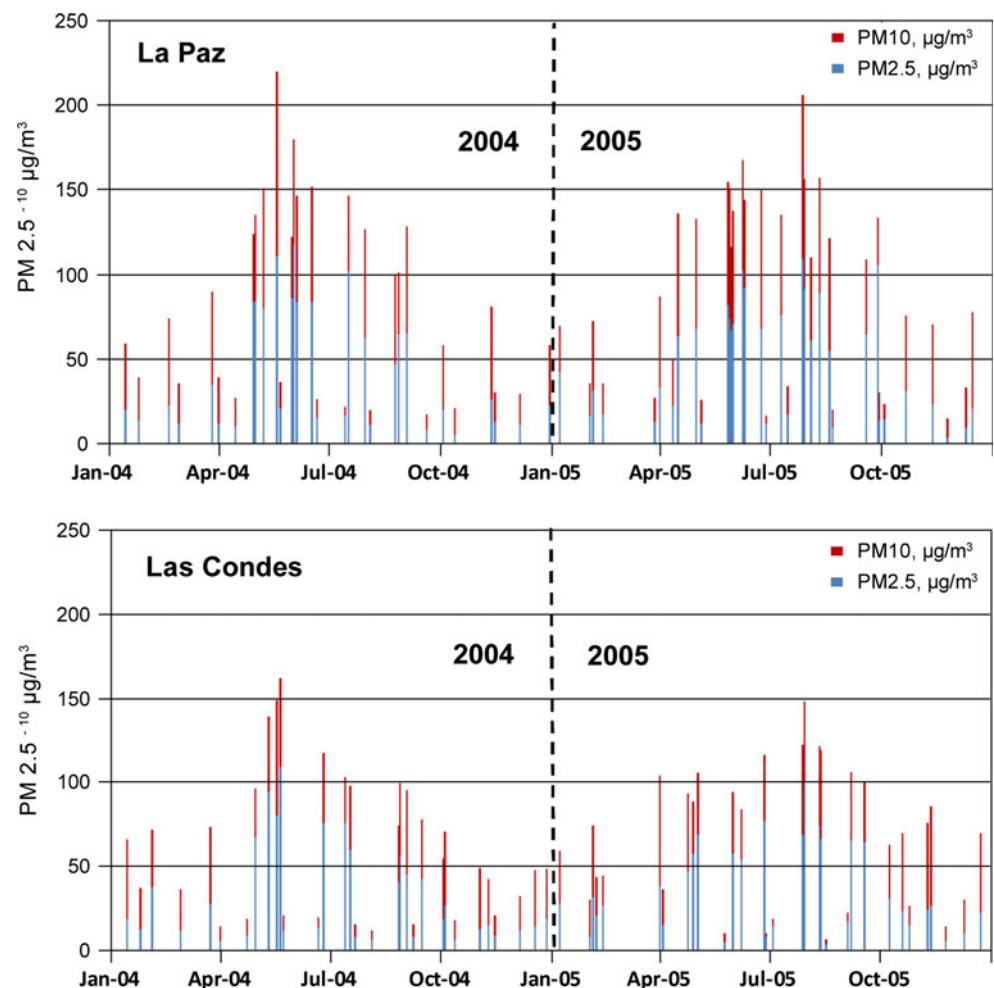
Variations between sites

Average inhalable particle (PM_{2.5} + PM_{10–2.5}) concentrations of the samples analyzed were 161.1 and $128.9 \mu\text{g m}^{-3}$ at LP and LC, respectively. Concentrations at LP were higher than at LC over both years. These concentrations are similar to those reported by Moreno et al. (2010) over the same years at the MACAM station of Parque O'Higgins (P.O), located in downtown Santiago to the south of the LP station.

Elemental concentrations

Santiago's PM_{2.5} concentrations during the cold season at the LP station show an enrichment of approximately 10 % in Pb and Zn and over 50 % in K, Ca, Ti, Cr, Mn, Fe, Ni, and Cu when compared with concentrations identified in central Mexico City (Miranda et al. 2004). Similarly, approximately 30 % higher Ca, Mn and Cu concentrations were measured at LP compared with Sao Paulo.

Fig. 3 Time series of PM_{2.5}–PM_{10–2.5} at LP and LC stations



Concentrations of the majority of the major and trace elements (Al, K, Cr, Fe, Ni, Zn, Sr, and Pb) were half those reported for Sao Paulo (Castanho and Artaxo 2001). Compared with Gent, Belgium (Maenhaut et al. 1996), Al and Ca concentrations in Santiago were approximately 80 % higher. Concentrations of Pb in Gent, however, were twice those found in Santiago (15.2 ng m^{-3}) and V concentrations were 20 times those measured in this study (0.5 ng m^{-3}). PM_{2.5} at the LP station in Santiago is enriched in Sb, As, Zn and Co by 72, 86, 35, and 98 %, respectively, compared with PM in Budapest (Salma and Maenhaut 2006).

Enrichment factors

In this study, enrichment factors (EFs) were used to identify related groups of elements, their abundances and provide an indication of potential PM sources.

Enrichment factors are calculated with respect to a conservative lithogenic element (typically Al, Zr or Th) and indicate the level of enrichment for all elements

compared with their average crustal abundances. EFs were calculated as follows:

$$EF_x = (C_x/C_{ref})_{\text{sample}} / (C_x/C_{ref})_{\text{crust}}, \quad (2)$$

where $(C_x/C_{ref})_{\text{sample}}$ is the concentration ratio of an element, x , to the reference element in the sample and $(C_x/C_{ref})_{\text{crust}}$ is the same ratio for typical crustal material.

The bulk average crustal abundances used were defined by Taylor and McLennan (1995). In this study, aluminum was used as a reference because of its crustal abundance in the area of the study (Vergara et al. 2004) and to its resistance to most surface processes. EFs higher than one suggest the contribution of a source(s) other than crustal matter, but a threshold of 10 is considered to be more reliable for discriminating between crustal and non-crustal origins (Parekh et al. 1989; Morata et al. 2008).

Based on reports by Reimann and Caritat (2000, 2005), the EF results were not used to identify anthropogenic and natural sources because the elemental reference values used in the normalization corresponded to average crustal surface concentrations. Also, the enrichment of certain elements in the crustal surface can be attributed to other factors. One of

Table 2 Main sources and their loadings identified in Santiago from factor analysis (FA) of the PM_{2.5} fraction

Station:	La Paz			Las Condes		
Number of factor:	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Principal contribution:	Natural Source crustal/sea	Cu smelting	Combustion process (oil/coal)	Cu smelting/ crustal	Natural Source crustal/sea	Combustion process (oil/coal)
Minor contribution:	Oil/coal combustion; copper smelter	Crustal origin; oil combustion		Oil/coal combustion;	Burning of biomass; oil combustion	
Elements						
Ag	0.32	0.72	0.10	0.68	0.58	
Al	0.89	0.26	0.22	0.55	0.70	0.17
As	0.18	0.88	0.21	0.86	0.20	0.31
Ba	0.52	0.76	0.18	0.87	0.38	0.23
Bi	0.30	0.83	0.35	0.89	0.29	0.27
Ca	0.82		0.42	0.21	0.85	0.25
Cd	0.34	0.84	0.30	0.90	0.21	0.30
Co			0.88			0.95
Cr	0.51	0.49	0.62	0.53	0.36	0.70
Cu	0.44	0.83	0.26	0.88	0.39	0.25
Fe	0.58	0.78		0.85	0.45	0.21
K	0.76	0.39	0.27	0.70	0.60	0.15
Mg	0.94	0.18	0.25	0.38	0.87	0.20
Mn	0.37	0.35	0.67	0.87	0.36	0.26
Mo	0.64	0.61	0.13	0.82	0.36	0.20
Na	0.91		0.19	0.34	0.91	
Ni	0.38	0.42	0.73	0.45	0.26	0.76
Pb	0.32	0.88	0.13	0.90	0.25	0.25
Rb	0.71	0.55	0.19	0.78	0.56	0.11
Sb	0.14	0.21	0.89	0.19		0.94
Sr	0.81	0.19	0.48	0.57	0.78	0.17
V	0.70	0.56	0.15	0.76	0.51	
Zn	0.55	0.36	0.54	0.52	0.40	0.63
Ti	0.76	0.58		0.68	0.59	0.19
Zr	0.74	0.18	0.14	0.74	0.57	0.11

Loadings ≥ 0.6 corresponded to natural sources (crustal matter and marine aerosol), copper smelting and combustion processes. Loadings < 0.6 corresponded to minor contributions

these factors is lithogenic variations from one location to another and another factor is differences in the biogeochemical cycles of some elements. The Earth's surface is composed primarily of biosphere and organic material, not the average crust (Reimann et al. 2008). Therefore, the behavior of the principal groups of elements identified is discussed in this study using a raw database and considering the impact of local sources on the sampling stations. The identification of anthropogenic and natural sources was performed using factor analysis and trace elements.

Factor analysis

It is important to verify that a dataset has a normal distribution and that measurements are independent of each

other prior to using factor analysis (FA). It is well-known among applied geochemists that regional geochemical data never show a normal distribution (Reimann et al. 2008) and that the presence of outliers in environmental studies is very common. Therefore, it is important that all variables have a near-normal distribution (Reimann et al. 2008) and that the impact of outliers is reduced by applying a robust FA (Filzmoser 1999; Pison et al. 2003). The identification and interpretation of PM sources is achieved through studying the factor scores produced.

FA has been used to identify the factors, or sources, contributing to measured PM concentrations (Table 2). Each factor demonstrates different elemental correlations that are indicative of specific sources (Reimann et al. 2008). The matrix loading values represent associations between each variable and each of the retained factors.

Table 3 Comparison of chemical signatures in Santiago

Sources	Natural sources		Anthropogenic sources			Sulfate/ secondary sulfate	Copper smelting	Biomass/Wood burning	Industry emissions
	Dust	Sea	Combustion	Oil	Coal				
Author and year of sampling									
Valdes ^a (2004, 2005)	PM_{2.5} : <u>Al, Ca, Fe, K, Rb, Sr,</u> <u>V, Ti, Zr, Ba, Cr, Mo,</u> <u>Zn</u>	PM_{2.5} : <u>Mg, Na</u>	PM_{2.5} : <u>Co, Cr, Mn,</u> <u>Ni, Sb, (Zn)</u>	PM_{10-2.5} : <u>Sb, Pb, As,</u> <u>Zn and Co</u>			PM_{2.5} : <u>Cu, Zn, As, Mo, Pb,</u> <u>Bi, Ag, Ba, Cd, Fe, K, Mn,</u> <u>Al, Cr, Rb, Sr, V, Ti, Zr</u>	PM_{2.5} : <u>K</u>	
Artaxo ^b (1996)	PM_{2.5} : <u>Al, Ca, Fe, Si, Ti, Sr,</u> <u>Mn (Pb, As, P)</u>		PM_{2.5} : <u>V, Ni, S, Zn, Cl, Mn</u>			PM_{2.5} : <u>S, Se, K, P</u>	PM_{2.5} : <u>S, Cu, Mo, As, K, P</u>	PM_{2.5} : <u>Zn, Cu</u>	PM_{2.5} : <u>Zn, Cu</u>
Moreno ^c (1998-2007)	PM_{10-2.5} : <u>Al, Ca, Si, Ti,</u> PM_{10-2.5} : <u>Fe, Mn,</u> <u>Mg, Sr</u>	PM_{2.5} : <u>Na, Cl</u> PM_{10-2.5} : <u>Na, Cl, (Mg)</u>	PM_{10-2.5} : <u>Mn, Cu, Fe, Zn, Pb</u> PM_{10-2.5} : <u>Ba, Cr</u>			PM_{2.5} : <u>S, P</u>	S		
Morata ^d (2004)	PM_{10-2.5} : <u>Al, Ca, Fe, Si</u>		PM_{10-2.5} : <u>FeO</u>			PM_{10-2.5} : <u>S, S-K/Ca S-</u> <u>(Fe, Mn, Cr,</u> <u>Ti)</u> SEM: <u>CaCO₃,</u> <u>CaSO₄, BaSO₄</u>	S		

Elements that were common to all studies are underlined, elements in bold have been considered to be typical of specific sources and elements in gray represent secondary elements typical of specific sources

Al aluminium, *Ca* calcium, *K* potassium, *Rb* rubidium, *Sr* strontium, *V* vanadium, *Ti* titanium, *Fe* iron, *Si* silicon, *Mn* manganese, *Mg* magnesium, *Na* sodium, *Ni* nickel, *S* sulphur, *Zn* zinc, *Cl* chloride, *Cu* copper, *Ba* barium, *Cr* chromium, *Br* bromine, *Pb* lead, *Se* selenium, *P* phosphorus, *As* arsenic, *Mo* molybdenum, *Bi* bismuth, *Ag* silver, *Cd* cadmium, *SEM* scanning electron microscopy

^a Valdes (this paper)

^b Artaxo et al. (1999)

^c Moreno et al. (2010)

^d Morata et al. (2008)

Table 4 Comparison of chemical signatures in central Chile

Sources	Natural sources		Anthropogenic sources			
	Soil dust	Sea salt	Combustion	Coal	Transport/automobile emissions/motor vehicle	Sulfate/secondary sulfate
			Oil			
Author and year of sampling						
Romo-Kröger ^a 1991 (Caletones-La Leonera)	Fine-coarse fraction: <u>Al</u> , <u>Ca</u> , <u>Fe</u> , <u>Si</u> , <u>K</u> , <u>Ti</u>					Fine-coarse fraction: <u>K</u> , <u>Ca</u> , <u>S</u>
Kavouras ^b 1998 (Rancagua)	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Al</u> , <u>Ca</u> , <u>Fe</u> , <u>Si</u> , <u>K</u> , <u>Ti</u> , <u>Sr</u> , <u>Mg</u>				<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Br</u> , <u>Pb</u> (<u>K</u> , <u>V</u> , <u>Fe</u> , <u>Ni</u> , <u>As</u> , <u>Cu</u> , <u>Mo</u> , and <u>Zn</u>)	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>S</u> , <u>Cu</u> , <u>Zn</u> , <u>As</u> , <u>Mo</u>
Kavouras ^b 1998 (Viña del Mar)	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Al</u> , <u>Ca</u> , <u>Fe</u> , <u>Si</u> , <u>Ti</u>	<u>PM</u> _{10-2.5} : <u>Cl</u>	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>S</u>		<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Br</u> , <u>Pb</u>	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Cu</u> , <u>Zn</u> , <u>As</u> , <u>Mo</u> , <u>Pb</u>
	<u>PM</u> _{10-2.5} : <u>Br</u> , <u>As</u> , <u>Cu</u> , <u>Zn</u> , <u>Pb</u> , <u>K</u>					<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>K</u> , <u>Fe</u> , <u>Rb</u> , <u>Sr</u>
Kavouras ^b 1998 (Valparaiso)	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Al</u> , <u>Si</u> , <u>Ca</u> , <u>Fe</u> , <u>Ti</u> , <u>Mn</u> , <u>Ba</u>	<u>PM</u> _{10-2.5} : <u>Cl</u>	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>S</u>		<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Br</u> , <u>Pb</u> (<u>K</u> , <u>Ca</u> , <u>Sr</u> , and <u>Ba</u>)	<u>PM</u> _{10-2.5} – <u>PM</u> _{2.5} : <u>Cu</u> , <u>Zn</u> , <u>As</u> , <u>Mo</u> , <u>Pb</u>
Hedberg ^c 1999–2000 (Quillota, Linares)	<u>PM</u> _{10-2.5} : <u>Al</u> , <u>Ca</u> , <u>Fe</u> , <u>Si</u> , <u>Ti</u> and <u>Mn</u>	<u>PM</u> _{10-2.5} : <u>Mg</u> , <u>Na</u> , <u>Br</u> , (<u>Ni</u> , <u>V</u> , <u>Cr</u> , <u>S</u>)	<u>PM</u> _{10-2.5} : <u>Ni</u> , <u>V</u>	<u>PM</u> ₁₀ : <u>Cr</u>	<u>PM</u> _{10-2.5} : <u>Br</u> , <u>Pb</u> , <u>V</u> , <u>N</u>	<u>PM</u> _{10-2.5} : <u>K</u> and <u>Zn</u> (<u>Rb</u>)

Elements that were common to all studies are underlined, elements in bold have been considered to be typical of specific sources and elements in *gray* represent secondary elements typical of specific sources

Al aluminium, *Ca* calcium, *Fe* iron, *Si* silicon, *K* potassium, *Ti* titanium, *Sr* strontium, *Mg* magnesium, *Mn* manganese, *Ba* barium, *Na* sodium, *Ni* nickel, *V* vanadium, *Br* bromine, *Pb* lead, *S* sulphur, *Cu* copper, *Zn* zinc, *As* arsenic, *Mo* molybdenum, *Ag* silver, *SEM* scanning electron microscopy

^a Romo-Kröger et al. (1994)

^b Kavouras et al. (2001)

^c Hedberg et al. (2005)

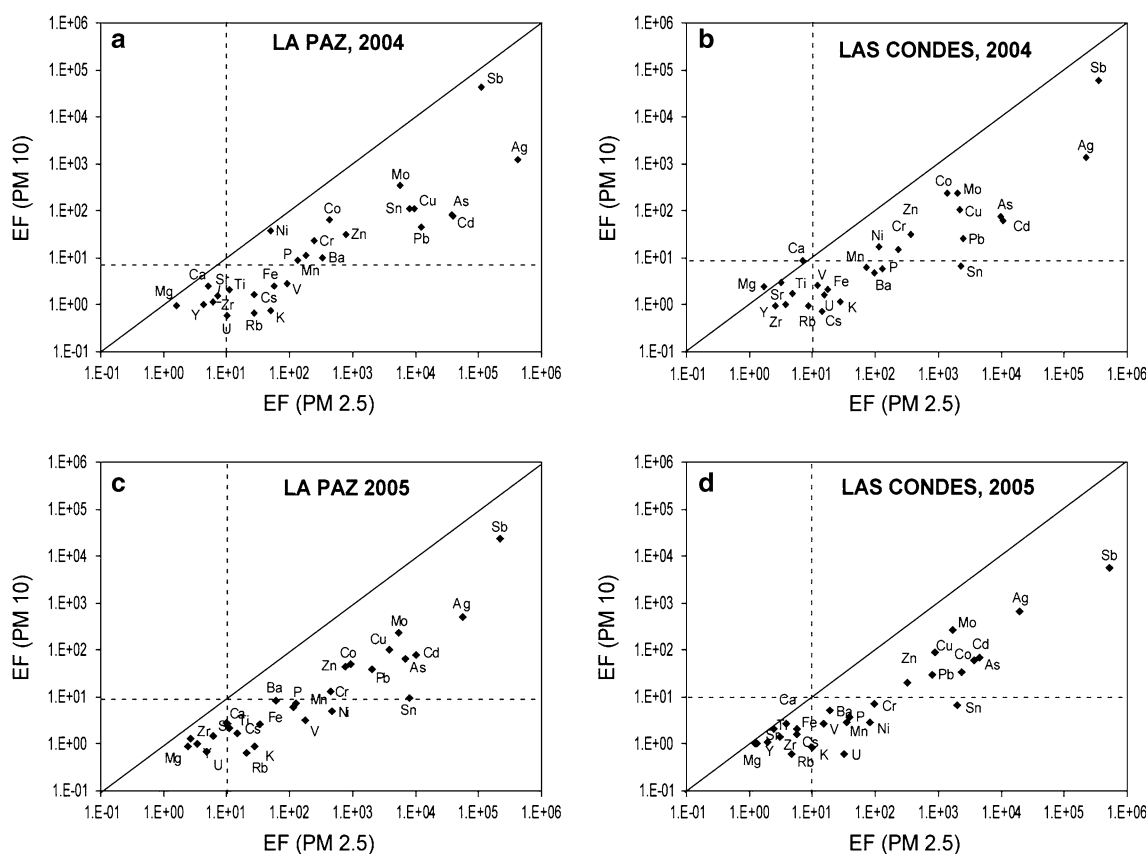


Fig. 4 Enrichment factors for $PM_{2.5}$ and $PM_{10-2.5}$ using Al as the reference element at La Paz (**a** and **c**) and Las Condes (**b** and **d**) in 2004 and 2005

This study identified three principal factors that explained 85 and 89 % of the total variance at LP and LC, respectively.

Adding to the FA, Tables 3 and 4 present the re-grouped major particle sources in Santiago and central Chile, as defined by previous authors. These sources were identified using FA. The sources were also classified according to their type and their geochemical characterization.

Rare Earth Elements (REE)

Kowalczyk et al. (1982) made the first observations of anomalous La enrichment and high La/Sm ratios in urban aerosols, identifying these elements as new tracers for specific anthropogenic sources. High La/Sm ratios were attributed to fluid catalytic crackers (FCC) in refineries that used zeolites. In general, zeolites are used as cracking catalysts in petroleum refineries in the USA, Europe and Japan (Kitto et al. 1992). These zeolites have significant light rare earth element (LREE) enrichment compared with the heavier, high rare earth elements (HREE), with La/Sm ratios as high as 300. These enrichments were also measured in the

volatile fraction of refined oils. These LREE enrichments (mostly La) were also measured in oil-fired power plants, without associated V enrichment. The two different sources could then be distinguished. A new LREE pollutant has been identified that comprises mostly Ce oxides that are used in the catalytic exhaust filters of new cars.

Particle origins

Chemical characterization and distribution of the elements

The elements Mg, Y, Zr, U, Sr, Ca, Ti, and V all showed $EF < 10$ in both particle size fractions at both sites in 2004 and 2005 (Fig. 4). The EFs for these elements were higher in $PM_{2.5}$ than in $PM_{10-2.5}$ at LP, while no such differentiation was apparent at LC. This indicates that different processes control PM emissions at the two sites and it is likely that the proximity of LP to combustion sources plays an important role in this.

Another group of elements (Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, and Zn) show moderate EFs (ranging from 10

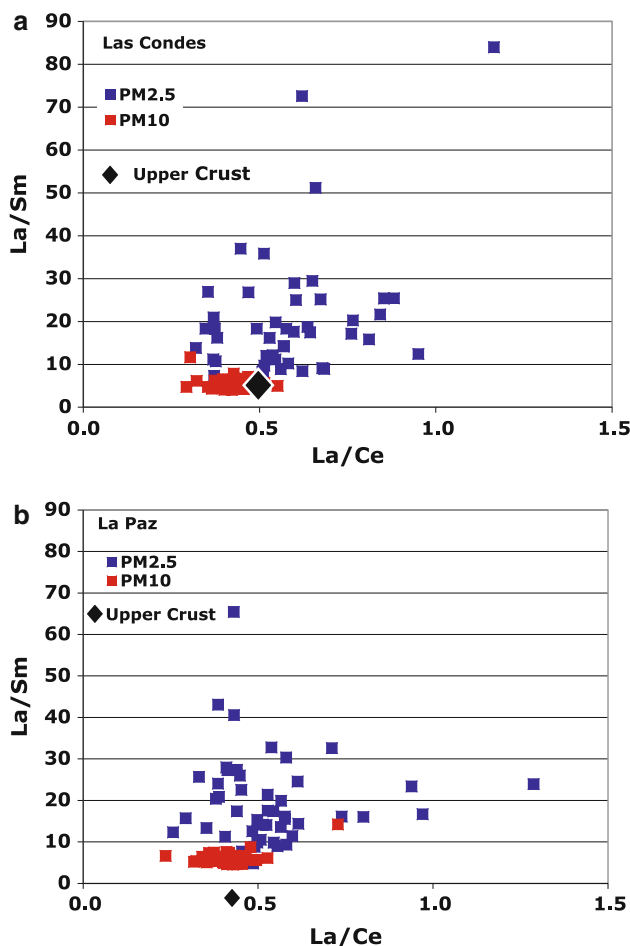


Fig. 5 Plots of La/Sm ratios versus La/Ce ratios in the PM_{10–2.5} and PM_{2.5} fractions at Las Condes (a) and La Paz (b)

to 10^3 and 10 to 10^2 for PM_{2.5} and PM_{10–2.5}, respectively). Finally, the highly enriched elements (Sn, Pb, Cu, Mo, Cd, As, Ag, and Sb) had EFs from 10^3 to 10^6 in the PM_{2.5} fraction.

Figure 4 presents the differences between enrichment levels in PM_{10–2.5} and PM_{2.5}. This is evident at both stations for all elements except Sb, suggesting that anthropogenic contaminants are released mainly as fine particles, probably through high-temperature processes as they favor small size particles (Morata et al. 2008).

Natural sources

FA of the PM_{2.5} fractions at both stations identified two natural sources. The first factor had high loadings (≥ 0.6) (Table 2) for the major elements Al, Ca, K, Mg, Mo and Na, and the trace elements Rb, Sr, V, Ti, and Zr, and loadings from 0.5 to 0.6 for Ba, Cr, Fe, and Zn. From these loadings this source was identified as crustal matter, which would include phyllosilicates, feldspars, pyroxenes, amphiboles and iron oxides. This is in agreement with

Morata et al. (2008) for two other sampling sites in Santiago and is in agreement with other studies (Artaxo et al. 1999; Moreno et al. 2010; Romo-Kröger et al. 1994; Kavouras et al. 2001; Hedberg et al. 2005) (Tables 3, 4).

The second source was identified to be marine aerosol because Na and Mg had high loadings (0.91, Table 2). Unfortunately, no data were obtained for Cl, which would have confirmed a marine aerosol source directly. The complicating issue is that Mg is found in some minerals such as pyroxene and amphibole (Morata et al. 2008), highlighting that Mg has a crustal origin. However, Na and Mg have been used to trace marine aerosols previously (Hedberg et al. 2005; Moreno et al. 2010). A positive correlation (~ 0.80) was identified between Mg and Na in both size fractions, suggesting a marine source.

Anthropogenic sources

Four anthropogenic sources at each station were identified using FA. The sources were copper smelting, coal/oil combustion, traffic and biomass burning. Three additional sources (catalytic converters, petroleum refining and power plants) were identified using rare earth elements.

The copper smelting source featured loadings ≥ 0.6 for Ag, As, Ba, Bi, Cd, Cu, Fe, Mo, and Pb, and loadings between 0.5 and 0.6 for Rb, V and Ti (Table 2). This signature is in agreement with previous results from central Chile (Table 4) that indicated Cu, Zn, As, and Mo were key tracers for copper smelters. Several studies have also shown the association of S and Pb with copper smelting (Romo-Kröger et al. 1994; Kavouras et al. 2001). Ag and Bi were also identified to be associated with copper smelting by Hedberg et al. (2005). Fe, Ba and Cd were identified to be first order elements associated with copper smelting. These elements are either present in the copper ores or are involved in the refining processes. The spherical morphology, around 1 μm in diameter, of some Fe, Zn, and Cu-bearing particles studied by SEM confirms that these particles are emitted during high-temperature processes (Morata et al. 2008).

A coal/oil combustion factor (Table 2) was identified based on high (≥ 0.6) Co, Cr, Mn, Ni, and Sb loadings. Moreno et al. (2007) suggested that Sb, Pb, As, Zn, and Co were related to coal combustion and could be used as tracers, despite low loadings for As (0.21) and Pb (0.13). Cr is also related to coal combustion (Hedberg et al. 2005). V and Ni are widely associated with oil combustion (Celis et al. 2004; Pey et al. 2009). Less frequently, Zn has been used as a tracer for oil combustion as well (Artaxo et al. 1999; Moreno et al. 2010). In this study, Ni had a high loading, but V did not, suggesting that oil combustion could have had only a small influence on this factor.

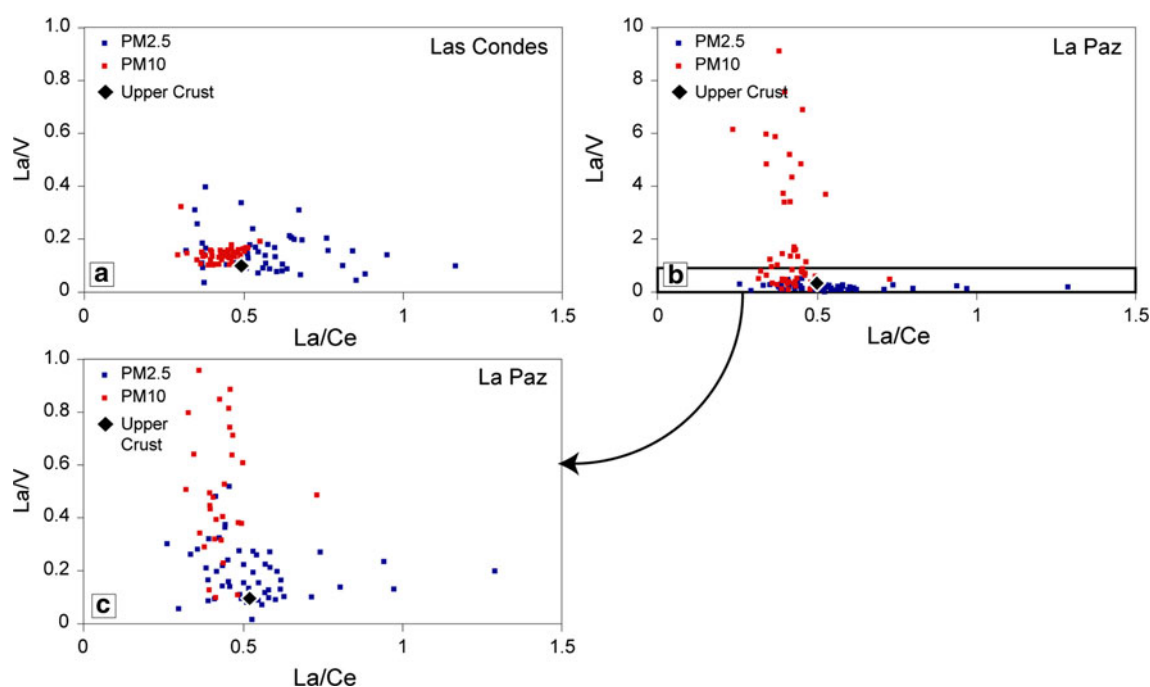


Fig. 6 Plots of La/V ratios versus La/Ce ratios at Las Condes (a) and La Paz (b). The La/V < 1 region at La Paz, which showed a similar pattern at Las Condes, is also shown in more detail (c)

The traffic factor was identified based on the presence of Mn. This is indicative of the combustion of unleaded gas featuring the organomanganese compound methylcyclopentadienyl-tricarbonyl-manganese, which is used as an anti-knocking agent (Celis et al. 2004). Typically traffic was traced by the association of Br with Pb (Tables 3 and 4), which would be expected for data collected before 2001 when leaded gas was still used. However, Pb would not be expected to relate to traffic emissions from 2004 to 2005. Using REEs as tracers for catalytic exhausts, and therefore traffic pollution, is recommended.

A biomass combustion source was identified based on high K and Rb loadings (0.5–0.6). Both elements are considered to be tracers of wood combustion (Carvacho et al. 2004; Celis et al. 2006; Kavouras et al. 2001). Hedberg et al. (2005) also suggested that Cr could be a tracer (Table 4).

Usually, when one compares chemical signatures of different sources, many elements appear to be related to more than one source. Therefore, one author might attribute an element to one of these sources, while others will attribute it to another source. For instance, in both stations, it is confirmed that Fe can be provided by two potential sources: copper smelting processes (as demonstrated through FA analysis) and/or natural lithogenic source, as already observed by Morata et al. (2008). Zn also shows this behavior as it appears in both places related to copper smelting and oil/coal combustion. Other examples are Cr,

Ni, and Mn, used as tracers of combustion process. However, in the area of study, there are volcanic and subvolcanic formations, where the mean concentrations are 893, 12, and 40 ppm for Mn, Ni, and Cr, respectively (Vergara et al. 2004). These geological units are probably sources of these elements. On the other hand, these values are below the average andesitic crust (Taylor and McLennan 1995). This interpretation is consistent with Iñigo et al. (2011) that observed in the soils of La Rioja, Spain mean values of Mn (738.2 mg kg^{-1}) on the surface and 550.7 mg kg^{-1} in depth, which suggests an origin from atmospheric deposition. However, the Ni concentrations have an opposite behavior where the mean values are 33.30 mg kg^{-1} on the surface and 40.49 mg kg^{-1} in depth, which suggests a lithogenic source.

Rare Earth Elements

Rare earth elements concentrations in the $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ fractions from the two sites are presented in Table 1. Maximum overall REE concentrations were 1.8 and 1.2 ng m^{-3} in $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$, respectively, at LP and 5.7 and 4 ng m^{-3} in $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$, respectively, at LC. These values were lower than those measured in Mexico, which were 10 ng m^{-3} (Moreno et al. 2008). In Washington and Delft, maximum REE concentrations were also approximately 10 ng m^{-3} (Moreno et al. 2008).

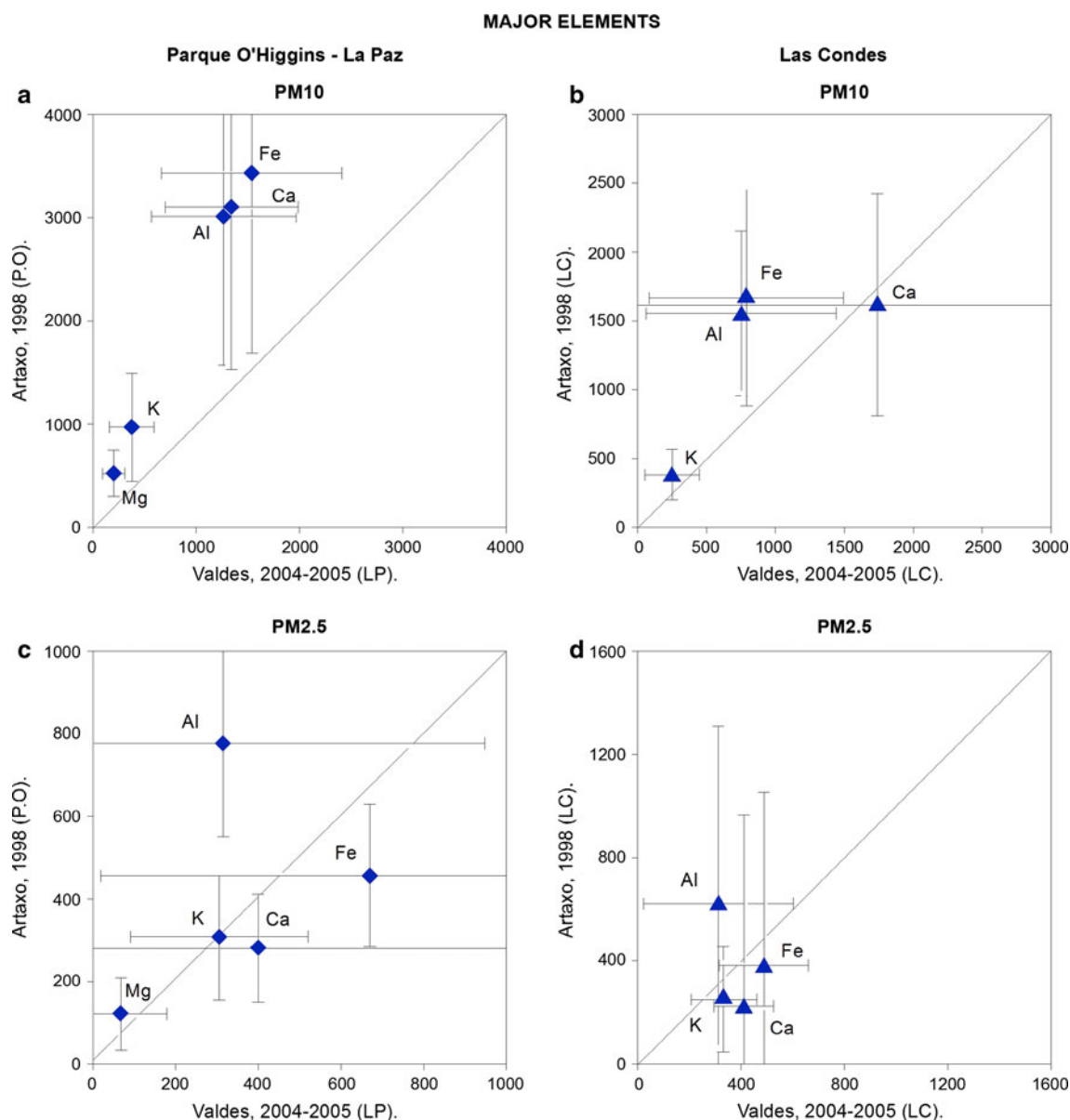


Fig. 7 Changes in the concentrations of major elements in $PM_{10-2.5}$ and $PM_{2.5}$ between 1998 at the P.O and LC stations (Artaxo 1998) and 2004–2005 at the LP and LC stations

Maximum REE concentrations measured in Philadelphia were approximately 50 ng m^{-3} , while those in Houston reached 90 ng m^{-3} (Moreno et al. 2008). REE pollution in Santiago appears to be relatively low compared with US cities, particularly Houston. REE concentrations are typically higher in $PM_{10-2.5}$ than in $PM_{2.5}$, which is an observation that still needs to be understood.

Catalytic converters

In Fig. 5, La/Sm ratios are plotted vs. La/Ce for the $PM_{10-2.5}$ and $PM_{2.5}$ fractions at LC (Fig. 5a) and LP (Fig. 5b).

In the $PM_{10-2.5}$ fractions at both sites La/Sm ratios are roughly constant at approximately 5, while La/Ce ratios vary from 0.28 to 0.55 and 0.22 to 0.52 at LC and LP, respectively. This indicates that La/Sm ratios remain close to “typical” crustal matter values, while La/Ce ratios show similar offsets from the crustal value (0.5) at the two sampling sites.

Conversely, in $PM_{2.5}$ fractions from both sites, the La/Sm and La/Ce ratios show distinct divergence from “typical” crustal matter. La/Sm ratios varied from 5 to 85 and 5 to 65 at LC and LP, respectively. La/Ce ratios varied from 0.23 to 1.56 and 0.28 to 1.3 at LC and LP, respectively. The enrichment of La and Ce is likely responsible for this.

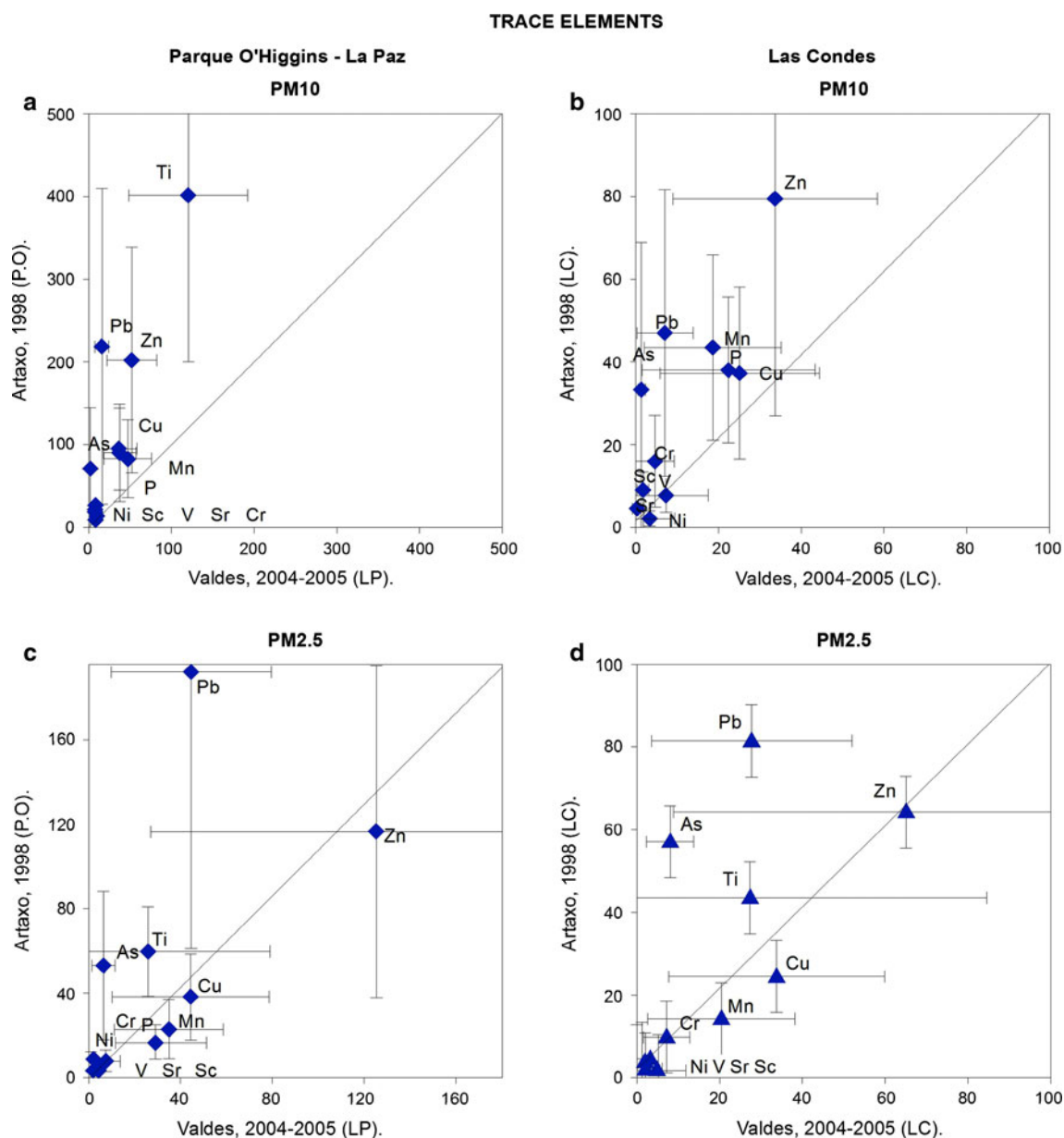


Fig. 8 Changes in the concentrations of trace elements in $PM_{10-2.5}$ and $PM_{2.5}$ between 1998 at the P.O and LC stations (Artaxo 1998) and 2004–2005 at the LP and LC stations

These results are indicative of contributions from Ce-oxide-rich catalytic exhausts (Moreno et al. 2008). The La/Sm ratios in $PM_{2.5}$ also show a signature typical of pollution from FCC or oil-fired power plants (Kowalczyk et al. 1982; Kitto et al. 1992).

FCC and oil-fired power plants

To more accurately identify the origins of the La and Ce enrichments discussed above, La/V ratios were plotted against La/Ce ratios (Fig. 6). Interestingly, the largest scatter and highest values are observed in the coarse

particle fraction. In fact, La/V ratios varied between 0.11 (crustal value) and 0.2 in $PM_{10-2.5}$ samples from LC and between 0.5 and 1.0 in some $PM_{10-2.5}$ fractions from LP. Conversely, La/V ratios in the $PM_{2.5}$ fractions varied from 0.04 to 0.4 and 0.05 to 0.2 at LC and LP, respectively. When analyzed as a function of time (not shown), the highest ratios were always found for filters collected during the winter, when PM concentrations are highest.

The high La/V ratios identified are indicative of FCC pollution (Moreno et al. 2008), but it was surprising that the highest La/V ratios were found in the $PM_{10-2.5}$ fractions, while the highest La/Sm ratios were in the $PM_{2.5}$

fraction. This pollution source was significant at LP, but was nearly non-existent at LC. One of the major thermoelectric plants in the Santiago region, which uses diesel and natural gas, is located 3.5 km west of the LP station and could account for the high La/Sm ratios measured. Previously there were no records of any FCC activities close to this station.

Meteorological consequences on the intensity and type of pollution

Eight daily samples in 2004 and six in 2005 corresponded to high pollution events associated with unfavorable meteorological conditions for pollutants dispersion, including low wind speeds, low altitude thermal inversions and a very low mixing layer. Low elemental concentrations were associated with high-pressure conditions (H, clear skies and sunny days), while higher concentrations were associated with before pre-frontal (BPF, cloudy days) and mixed (BPF-H) systems. Wind direction varied during transitions from one system (BPF) to the other (H). This transition was usually facilitated by westerly winds which transported PM from the ocean to the land, and may be responsible for increased Na and Mg concentrations.

During these specific meteorological conditions, Cu, Mo, As, and Zn concentrations in $PM_{2.5}$ at both stations peaked. For example at LC these elements had concentrations of 72.2, 5.14, 10.6, and 187.2 $ng\ m^{-3}$, respectively. At LP, these conditions resulted in arsenic concentrations that were three times greater than health standards.

Evolution of elemental concentrations in $PM_{10-2.5}$ and $PM_{2.5}$ between 1998 and 2004/2005

Results from this study (2004–2005) were compared with results from 1998 at LC and Parque O'Higgins (PO) (Artaño 1998). The PO and LP were both in downtown Santiago, though the LP site was in a more industrial and densely populated area than the PO site.

Major elements

$PM_{10-2.5}$

Many major element concentrations measured in $PM_{10-2.5}$ at the LP station decreased significantly, including Fe (3,430–1,530 $ng\ m^{-3}$), Ca (3,104–1,336 $ng\ m^{-3}$), Al (3,010–1,261 $ng\ m^{-3}$), K (975–371 $ng\ m^{-3}$), and Mg (531–195 $ng\ m^{-3}$) (Fig. 7). These decreases were likely in relation to different environmental policies introduced,

which were detailed in the “Introduction”. A similar trend was also observed at the LC station (Fig. 7), with exception of Ca concentrations, which slightly increased from 1617.16 to 1738.3 $ng\ m^{-3}$. This result is consistent with increased development in the city and a boom in the building industry totaling 4.2 % annually, explaining the annual Ca concentration increase of 6.4 % from 1998 to 2007 (Moreno et al. 2010).

$PM_{2.5}$

Among the elements whose concentrations decreased in the $PM_{10-2.5}$ fraction, only aluminum (776–316 $ng\ m^{-3}$) and magnesium (121–68 $ng\ m^{-3}$) concentrations decreased at LP in the fine fraction (Fig. 7). Ca and Fe concentrations increase by approximately 45 %. At LC, the increases were approximately 80 % for Ca and 26 % for Fe, while K (300 $ng\ m^{-3}$) concentrations were almost constant. These increased concentrations were related to increased human activities.

Trace elements

$PM_{10-2.5}$

In downtown Santiago (Fig. 8), trace element concentrations in the coarse fraction decreased by more than 50 %. These decreases included elements like Pb (219–15 $ng\ m^{-3}$), Zn (203–52 $ng\ m^{-3}$), As (70–2 $ng\ m^{-3}$), Cu (90–37 $ng\ m^{-3}$), Mn (95–37 $ng\ m^{-3}$) and Ni (4–2 $ng\ m^{-3}$). These decreasing trends are likely related to the current air quality improvement programs in Santiago. A similar trend was also observed at LC, where Cu concentrations decreased from 37 to 25 $ng\ m^{-3}$ and Ni concentrations remained constant at 3 $ng\ m^{-3}$.

$PM_{2.5}$

At both stations, V, As and Pb concentrations decreased between 65 and 85 %. For example, at LP, V concentrations decreased from 7 to 1 $ng\ m^{-3}$, As concentrations decreased from 49 to 7 $ng\ m^{-3}$ and Pb concentrations decreased from 177 to 45 $ng\ m^{-3}$ (Fig. 8). The 73 % decrease in V concentrations was because of industrial emissions reduction plans (Lents et al. 2006). Both stations showed slight increases in the concentrations of some elements like Cu and Mn at LP and Zn, Cu, and Mn at LC. Ni (2.10 and 5.12 $ng\ m^{-3}$) and Cr (7.16 $ng\ m^{-3}$) concentrations were almost constant from 1998 to 2005. Decreasing Pb concentrations were the result of the introduction of unleaded gasoline (Sax et al. 2007). Ni and Cr are related to oil and coal combustion, respectively, and their release into the atmosphere is from the gradual

replacement of gasoline by diesel and liquid petroleum gas since 2004 (Speiser 2007). Relatively constant or slightly increasing concentrations of Cu, Zn, and Mn highlight the regional impact of different copper smelters around Santiago. This is also consistent with the fact that since 2000 Chile has led the international copper market in terms of refined copper production, with more than 1 million tons/year and 5 % annual growth (Cochilco 2006). Peak concentrations of these metals from 2004 to 2005 occurred during the cold season, and were coincident with general atmospheric systems that were characterized by prefrontal conditions of low pressure and temperature, associated with cloudy days with weak winds.

Conclusions

Natural and anthropogenic PM sources affecting Santiago have been identified using a larger set of elements than in previous studies. Quantifying REE concentrations is becoming increasingly important because REEs are frequently used in industrial processes and catalytic converters. Because traffic sources cannot be traced using lead anymore, REE ratios could become valuable traffic source tracers. This type of pollution could increase over the next decade and should be controlled. These preliminary results could be useful as reference values in future investigations.

Both particle size fractions had higher concentrations of major and trace elements during cold seasons and the highest concentrations were measured at the LP station in the center of the city. Using enrichment factors, the elements Mg, Y, Zr, U, Sr, Ca, Ti, and V were identified to have a crustal origin ($EF < 10$), while Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn, Sn, Pb, Cu, Mo, Cd, As, Ag, and Sb ($EF > 10$) had anthropogenic origins. Three main sources were identified using factor analysis: natural sources (crustal matter and marine aerosol), oil/coal combustion and copper smelting.

The results show that concentrations of Fe, Ca, Al, K, and Mg in $PM_{10-2.5}$ have decreased since 1998 (Artaxo et al. 1999), while concentrations of Ca and Fe in $PM_{2.5}$ have increased by 80 and 40 %, respectively. These increases were likely related to more construction and smelting activities.

Trace element concentrations in $PM_{10-2.5}$, including Pb, Zn, As, Cu, Mn, and Ni decreased since 1998, while only V, As, and Pb concentrations decreased in $PM_{2.5}$. Cu, Mn, and Zn concentrations in $PM_{2.5}$ increased, while Ni and Cr concentrations remained relatively constant. The general decrease of PM and elemental concentrations over the last decade is likely because of public policies implemented. However, increasing Cu, Mn, and Zn concentrations are concerning and it seems necessary to improve controls on

specific elements, especially in $PM_{2.5}$. For example, As concentrations in $PM_{2.5}$ were three times higher than standard concentrations under specific meteorological configurations (H-BPF and BPF).

$PM_{2.5}$ concentrations measured in Santiago were below those measured in Sao Paulo, but were double those measured in Mexico City. In many cases, they exceed the concentrations experienced in European urban centers. This highlights the importance of better $PM_{2.5}$ management in Santiago.

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